

Appendix A

Summary of Analytical Methods, Quality Assurance, and Quality Control for Field Sampling and Laboratory Water Quality Analysis 2005-2007

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Introduction

In 2005, 2006, and 2007, nearly 2000 water samples were collected along the San Joaquin River (SJR) and major tributaries by the Environmental Engineering Research Program (EERP) located at the University of the Pacific (UOP) in support of the DO TMDL project. During sample collection field measurements were taken including water velocity, chlorophyll fluorescence, specific conductivity, pH, dissolved oxygen, oxidation-reduction potential and turbidity, solar radiation, TDS, temperature, sonde depth, and barometric pressure. Vertically integrated water grab samples were collected and brought to the EERP laboratory for immediate processing. Two sampling teams were deployed to insure all sites were sampled during the same day to allow for consistent environmental conditions for all samples. At the EERP laboratory samples were filtered, analyzed, or preserved within 24 hours of sample collection. Samples were transported to University of California, Davis (UCD) on the sampling day and filtered, analyzed, or preserved in the lab within 24 hours.

The purpose of this report is to describe the performance of the analytical and field crew and the quality of the data set as defined in the DO TMDL Quality Assurance Project Plan (QAPP) (Stringfellow, 2005). For the purpose of this report, Quality Assurance (QA), as outlined in the QAPP, is the process in which the project data is evaluated and handled. Quality Control (QC) guidelines are the requirements specified in the QAPP to determine if the data is valid. The QAPP provides both a QA process and QC requirements for production of accurate and precise water quality analysis from the laboratory and the field in support of the project objectives. The QAPP imposes several layers of quality review on the data. These include procedures established for data collection and processing by the laboratory analyst and the field personnel; oversight by the QA/QC manager; review by data analysts; and review by independent personnel. This iterative process has helped create a complete and high quality data set.

Methods

Data Quality Assurance and Quality Control

Each analytical group (UC Davis or EERP) has established Standard Operating Procedures (SOPs) (Borglin et al., 2005) for all routine analysis methods. The SOPs insure consistency in the analysis procedures, data reporting, and QC requirements. The SOPs were prepared by experienced analysts in collaboration with the QA/QC manager. The SOPs were kept in the analysis area and a master copy was kept on file. Daily laboratory work at the bench level was carried out according to these documents.

Data produced daily by analysts was recorded electronically and in a laboratory notebook. Electronic forms were used for entering data and calculation of results from the unknown samples and standards using calibration parameters. Preliminary review of data quality was completed by the analyst who confirmed that all standards and quality control samples met quality control guidelines. If the guidelines were not met, the analyst met with the QA/QC manager to identify the problem and the samples were then re-analyzed after remediation of any problems with analytical instrumentation, standards, calibration, or analysis procedures. Data that passed QC guidelines was then entered into the master spreadsheet.

Data in the master spreadsheet was subject to further review by applying simple linear regressions between correlated analyses to identify data outliers. This procedure was used to check for data entry or calculation errors. If problems were discovered during this process, the analyst was asked to recheck the data entry and quality of the sample analysis.

Quality control procedures for each laboratory analysis, discrete field sampling events, and continuous field monitoring data collection include calibration of instruments with certified standards. Quality control samples were run in conjunction with unknown samples and, depending on the analysis, could include all or some of the following: calibration check standards, laboratory control samples, sampling and analytical duplicates, matrix spikes, and analytical blanks (Table 1). In addition, analyses of performance test standards were conducted at a minimum of once a year to verify the proper working order of equipment, quality of reagents, analytical technique, and analytical methods.

Sampling and Field Water Quality Measurements

Field sampling consisted of collecting water samples, measuring water quality with a sonde, and recording of field conditions at sites within the study area. Prior to sampling, field equipment was calibrated (see below) and trip blanks were gathered and loaded into the sampling vehicles. Field sheets describing the sampling routine were disseminated before sampling to the sample crew and other pertinent individuals. Sampling was attempted at each site on the field sheets the day of sampling. At each site, water and water quality measurements were collected. The samples were stored at 4°C after collection and returned to the lab for analysis.

The day before sample collection YSI 6600 Sonde connected to YSI 650 MDS handset were calibrated at EERP following procedures in the YSI 6-Series Environmental Monitoring Systems Handbook (YSI Inc., Yellow Springs, CO). The sonde has several probes which were calibrated independently. Dissolved oxygen and depth were calibrated using the wet-towel method where the sonde was placed in a tube with a wet-towel around the sensors and calibrated in a water-saturated air environment. Specific conductance, measured with a temperature compensated electrical conductivity probe (EC), was calibrated using a 0.01D KCL conductivity standard with a value of 1408 μ S/cm (Radiometer Analytical SAS, Lyon, France). Temperature calibration is checked against a NIST certified thermometer. The pH probe was calibrated using standards of pH 4, pH 7, and pH 10 (VWR International, West Chester, PA). Oxidation-reduction potential (ORP) was calibrated with Zobell's solution (Ricca Chemical Company, Arlington, TX). The fluorescence probe output (for estimating chlorophyll) was recorded in Millipore water or 0 NTU water to account for drift. The turbidity probe was calibrated with three standards of 0 NTU or Millipore water, 40 NTU, and 200 NTU (HACH, Loveland, CO).

Each sampling day, the sonde was recalibrated for dissolved oxygen at the first site to correct for ambient barometric pressure. At each sampling location, water quality data was collected for at least 2 minutes using a sonde deployed in the sample water and programmed to measure and record every parameter every four seconds, providing a statistically significant sample size ($n > 30$). The data from the sonde was also recorded in the field notebook. The parameters measured by the sonde at each site included time, temperature (°C), specific conductance (mS/cm), total dissolved solids (g/L), dissolved oxygen (DO), DO concentration

(mg/L), DO charge, depth (ft), pH, oxidation-reduction potential (mV), turbidity (NTU), chlorophyll content ($\mu\text{g/L}$), fluorescence, and barometric pressure (mmHg).

While the sonde logged water quality data, water samples were collected and incident sunlight and water velocity were measured to document current field conditions. During sampling in 2005, the Photosynthetically Active Radiation (PAR) was measured in triplicate in full sun mode using a LI-250A meter with the LI-192 underwater quantum sensor and LI-193 spherical quantum sensor (Li-cor, Lincoln, NE). Light measurements were also taken using a Model 3252 (LUX) Traceable® Dual-Display Light Meter (Control Company, Friendswood, TX). It was found that the readings between the model 3252 and the LI-192 were highly correlated in 2005 and only the LUX meter readings were taken in 2006 and 2007. For 2006 and 2007, each LUX meter was independently correlated to the PAR meter and PAR was calculated from the LUX measurements. Velocity measurements were taken with a Marsh-McBirney Model 2000 Flo-Mate (Marsh-McBirney, Frederick, MD) with the velocity sensor facing upstream and horizontal to the water flow.

Water samples were collected in glass 1000 mL bottles (Wheaton Science Products, Millville, NJ), 1000 mL HDPE Trace-Clean narrow mouth plastic bottles (VWR International), 250 mL HDPE Trace-Clean wide mouth plastic bottles (VWR International), as well as 40 mL trace clean vials with PTFE septa (ICChem, Rockwood, TN) in accordance with requirements for different lab analyses and volume requirements. Bottles were labeled with the appropriate sample number, site name, and sampling date. All bottles were rinsed with sample water prior to collection of a depth-integrated sample. Some sites required a bucket to collect sample water because of accessibility from a high bridge or platform. For these sites, the bucket was pre-rinsed with sample water and sample bottles were filled using a rinsed funnel. Care was taken to distribute water simultaneously to all sample bottles (rather than sequentially). Samples were immediately stored at 4°C after sampling (cooler temperature was recorded in the lab upon delivery) and transported to the lab on the day of sampling. All bottle numbers, meter readings, and time in and out of the sample site were recorded in the field notebook.

Post field activities included cleaning and storing all field equipment and post-calibrating the sondes to account for drift during the sampling day. Post-calibration consisted of checking the sonde value to that of the standard value and was completed within twenty-four hours of the sampling event. After post-calibration sondes were cleaned and stored with a small amount of water in the calibration cup to prevent drying of the DO membrane.

Sample preparation and processing

Samples were received by the laboratory the same day they were sampled, logged in and inspected for damage, and stored at 4°C until filtering and analysis. Samples were filtered and preserved if necessary within 24 hours of collection. Archive filtrate and unfiltered samples were saved from all sites for any needed re-analysis or additional analysis that may be determined necessary. Samples were analyzed in laboratories at both EERP and UC Davis, and the procedures are described separately below.

Samples were collected, preserved, stored, and analyzed by methods outlined in *Standard Methods for the Analysis of Water and Wastewater*, (APHA, 2005, 1998) unless otherwise indicated. Certified standards, trace clean and certified sample bottles, reagent grade chemicals, and high purity water produced by a Milli-Q gradient system (Millipore, Billerica, MA) were used for all analyses. Reused glassware was cleaned thoroughly within warm water with Alconox detergent, rinsed with 10% HCl, and rinsed a minimum of 5 times with high purity de-ionized water.

UC Davis

Samples for dissolved nitrate, ammonia, and phosphate ($\text{NO}_3\text{-N}$, soluble $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$) were filtered through a pre-rinsed, 0.22 μm polycarbonate membrane (Millipore IsoporeTM). $\text{NO}_3\text{-N}$ and soluble $\text{NH}_4\text{-N}$ were quantified simultaneously using an automated membrane diffusion/conductivity detection method (Carlson, 1978, 1986; Carlson et al., 1990). Total nitrogen was determined by the same method from unfiltered sample following persulfate oxidation (Yu et al., 1994) using a 1% persulfate oxidant concentration, a sample:oxidant ratio of 1:1 (V/V), and heating in an autoclave. The limit of detection for this method was 50 ppb N.

Ortho-phosphate ($\text{PO}_4\text{-P}$) was determined on the filtrate using the stannous chloride method. (SM 4500-P.D). The limit of detection for this method is approximately 3 ppb $\text{PO}_4\text{-P}$ in clean water using a 1 cm cell for measurement. Total phosphorus (Tot P) was analyzed on unfiltered samples by the same method after digestion. To digest, 5.0 mL of each sample was aliquotted into trace clean, 5.0 mL digestion reagent (10 g potassium persulfate, 6 g boric acid, and 3 g NaOH in 1000mL Millipore water) was added and then was autoclaved for 1 hour. After cooling, Tot P was determined using the stannous chloride method as described above.

EERP

Filters were used in the analysis of chlorophyll pigments, particulate organic matter (samples sent to USGS for analysis), total suspended solids and volatile suspended solids (TSS/VSS), and phospholipid fatty acid analysis (PLFA). Sample for $\text{NO}_3\text{-N}$, $\text{PO}_4\text{-P}$, and dissolved organic carbon (DOC) were filtered through 47mm Whatman GF/F filters (0.7 μm pore size) for the collection of filterable solids. Filters used for TSS/VSS analysis were pre-rinsed with high purity water (Milli-Q gradient, Millipore, Billerica, MA). All filters were pre-combusted for 6 hours at 550°C prior to filtering. Sample bottles were shaken thoroughly before filtration and sample bottle weights were recorded before and after the sample was filtered and the difference was recorded as the filtered sample weight. Samples for dissolved Si ($\text{SiO}_4\text{-Si}$) were filtered through a pre-rinsed 0.45 μm pore size cellulose luer-lock syringe filter (Nalgene, Rochester, NY) within 24 hours of collection and stored at 4°C until analysis.

Unfiltered samples were analyzed for biochemical oxygen demand (BOD) by Standard Method (SM) 5210 B (APHA, 2005) with a modification for measurement of oxygen demand at 10 days rather than 5 days. Previous studies in the SJR have used 10-day BOD analysis as a standard procedure and this data set will be consistent with prior studies. BOD was measured without seed, as in previous studies. Initial and final dissolved oxygen was

measured using a calibrated YSI 5000 DO meter equipped with a YSI 5010 BOD probe (Yellow Springs, OH) and calibrated by Winkler titration according to SM 10200 H (APHA, 2005). Duplicate samples were prepared every 20 analyses and blanks consisted of BOD buffer solution prepared according to SM 5210 B. All samples were analyzed at both full concentration and diluted 100 mL of sample to 200 mL of BOD buffer solution to increase the number of reportable results. All BOD analyses were initiated within 24 hours of sample collection. A standard curve was prepared for each sample set consisting of a BOD standard solution (HACH, Loveland, CO) containing glucose and glutamic acid at 1, 2, 3, and 4 mg/L in dilution buffer with 5 mL of seed from a randomly selected sample. In addition, carbonaceous BOD (CBOD) was determined by adding 0.16 mg of nitrification inhibitor (N-serve, HACH, Loveland, CO) to a duplicate sample set. The resulting CBOD was subtracted from the total BOD to determine the nitrogenous BOD (NBOD). The limit of detection for BOD, CBOD, and NBOD is 1.0 mg/L.

Total organic carbon (TOC), inorganic carbon (IC), and DOC were analyzed on a Teledyne-Tekmar Apollo 9000 (Mason, OH) by high temperature combustion according to SM 5310 B (APHA, 2005) and quantified using a NDIR detector. TOC and IC were analyzed on unfiltered samples and DOC was analyzed on filtered samples. This machine was equipped with an auto-sampler that allows for continuous stirring of sample. Both DOC and TOC samples were preserved at less than pH 2 with concentrated H_3PO_4 and stored at 4°C until analysis. IC samples were collected in the field into vials preserved with no head space, 5-10 mg CuSO_4 powder and stored at 4°C until analysis. Samples were analyzed within 28 days of collection. The limit of detection for TOC and DOC is 1 mg/L C and for IC it is 5 mg/L.

Total suspended solids (TSS) and volatile suspended solids (VSS) were analyzed by SM 2540 D and E (APHA, 2005). Typically 1000 mL of sample was filtered on pre-weighed, pre-combusted, Whatman GF/F filters. The filters were placed in an aluminum dish and dried at 105°C under vacuum to constant weight. After drying, the filter and dish were allowed to cool in a dessicator and were weighed for TSS determination. The dried and weighed filters were subsequently combusted at 550°C for 6 hours and reweighed for VSS determination. Mineral suspended solids (MSS) concentration was calculated by subtracting VSS from TSS.

Chlorophyll-*a* (chl-*a*) and pheophytin-*a* (pha-*a*) were extracted and analyzed using UV absorption as described in SM 10200 H (APHA, 2005). Both the trichromatic chl-*a* and the pha-*a* methods were used for quantification. Approximately 1000 mL of samples were filtered using a vacuum filtration onto a Whatman GF/F filter within 24 hours of sample collection. The sample was kept in the dark during storage and filtration. After the water was removed saturated MgCO_3 was applied to the sample on the filter and the filter was stored at -20°C for up to 21 days before analysis. Extraction was performed by grinding the filter with a Teflon tissue grinder in acetone saturated with 10% by weight MgCO_3 . The extracted sample was centrifuged for 20 minutes at 2000 rpm and the chl-*a* and pha-*a* was quantified by measurement of the supernatant on a Perkin Elmer Lambda 35 spectrometer (PE Spec) using a 5 cm path length cuvette (Wellesley, MA).

For PLFA analysis, up to 1000 mL of water sample was filtered through a Whatman GF/F glass fiber filter within 24 hours of collection. After filtration, the filter was placed in a 25 mL glass tube or in foil packets and stored at -20°C until extraction. Total lipids and chlorophyll pigments were extracted from the filter with a modified Bligh-Dyer solution

which consists of 5 mL of chloroform, 10 mL of methanol, and 4 mL of phosphate buffer. Chlorophyll pigments in the extract were quantified by measuring absorbance at 665 nm on the PE Spec. Extracted lipids were methylated with an alkaline methanol reagent and quantified on Agilent Model 6250 (Santa Clara, CA) gas chromatograph equipped with both a flame ionization and mass spectrometer detectors.

Total protein was quantified in all the samples using the Lowry method (Pierce Biosciences, Rockford, IL). The analysis was scaled up from the standard kit so the analysis was performed on 1 mL samples and analyzed in cuvettes with a 5 cm path length. Standard curves were made using bovine albumin from Pierce Biosciences (Rockford, IL). Samples were frozen within 24 hours of collection and defrosted prior to analysis. The limit of detection for this analysis is 0.5 mg/L Protein.

Alkalinity was measured on samples within 24 hours of sample collection by titration of a 50 mL sample with 0.02 N H₂SO₄ to an endpoint of pH 8.3 and 4.5. The samples were stirred continuously during titration. Quality control included analysis of two independent alkalinity standards, one from HACH (Loveland, CO) and the other from ERA (Arvada, CO), to insure proper preparation of the titrating solution and calibration of the pH probe. The limit of detection for this method is 2.0 mg/L CaCO₃.

Total Iron (Tot Fe) was measured using a reaction with phenanthroline according to SM 3500-Fe B using FerroVer reagents purchased from HACH (Loveland, CO). Within twenty-four hours of sample collection, 6 mL aliquots of unfiltered sample was placed in 15 mL disposable centrifuge tubes and stored at -20°C for later quantification of Tot Fe. Prior to analysis, the samples were defrosted and 1 mL of sample was removed and used to measure the background absorbance of the water sample at 510 nm on the PE Spec. Total Fe was measured on the remaining 5 mL of unfiltered sample by the addition of pre-made HACH FerroVer phenanthroline reagent and measurement at 510 nm. The background sample absorbance was subtracted from the sample absorbance with reagent added. The limit of detection for this method is 0.05mg/L Fe.

Total ammonia nitrogen (Tot NH₄-N) was quantified with the Nesslerization method (SM 4500-NH₃ C, APHA, 1992) modified for use on SJR samples. The analysis was performed on unfiltered samples that were frozen within 24 hours of collection. After defrosting, 5 mL of sample was centrifuged at 3000 rpm for 5 minutes. Background interference from sample color was determined by measurement of 0.5 mL of the supernatant 425 nm prior to the addition of reagent. HACH Nessler reagent (Loveland, CO) was then added to the remaining sample; the sample was vortexed thoroughly and re-centrifuged (to remove interference from salts). Ammonia was quantified by subtracting the absorbance of the sample without reagent from the sample with reagent at 425 nm. The reportable limit for this method was 0.32 mg/L NH₄-N.

Starting in 2007 total ammonia nitrogen (Tot NH₄-N), dissolved nitrate (NO₃-N), and total nitrogen (TN) were quantified using the TL-2800 ammonia analyzer made by Timberline Instruments (Boulder, CO). The Tot NH₄-N analysis was performed on unfiltered samples that were frozen within 24 hours of collection. The reportable limit for this method is 0.045 mg/L NH₄-N. The NO₃-N analysis was performed on filtered samples that were frozen within 24 hours of collection. The reportable limit for this method is 0.08 mg/L NO₃-N. The TN analysis was performed on digested unfiltered samples that were frozen within 24 hours of

collection. To digest samples, 5.0 mL of each sample was aliquotted into trace clean 16x150 glass tubes with PTFE lined caps (VWR International), 5.0 mL digestion reagent was then added (10 g potassium persulfate, 6 g boric acid, and 3 g NaOH in 1000mL Millipore water), and samples were autoclaved in a Tuttnauer Brinkman autoclave (Westbury, NY). After cooling, TN was determined using the nitrate electrode method as described above. The reportable limit for this method is 0.14 mg/L TN.

Dissolved Si ($\text{SiO}_2\text{-Si}$) concentration was determined using a modified Heteropoly Blue molybdosilicate method (modified SM 4500- SiO_2 D) using Hach reagents (Loveland, CO). Dissolved Si was measured in filtered samples at both 650 and 815 nm using the PE Spec. The reportable limit for this method is 0.05 mg/L $\text{SiO}_2\text{-Si}$.

Dissolved ortho-phosphate ($\text{PO}_4\text{-P}$) was quantified in filtered samples by the ascorbic acid method (adapted from SM 4500-P-E) using HACH PhosVer3 packets (Loveland, CO) and measurement at 890 nm on the PE Spec. The reportable limit for this method was 18 $\mu\text{g/L}$ $\text{PO}_4\text{-P}$.

Combined nitrate ($\text{NO}_3\text{-N}$) and nitrite ($\text{NO}_2\text{-N}$) nitrogen were analyzed by the cadmium reduction method (adapted from SM 4500- $\text{NO}_3\text{-E}$) using HACH NitraVer (Loveland, CO) reagents. The reportable limit for this method was 0.5 mg/L $\text{NO}_3\text{-N}$.

Total phosphorus (Tot-P) was determined on 5.0 mL of unfiltered sample by persulfate digestion and colorimetric determination by the ascorbic acid method (adapted from SM 4500-P B, E). To digest samples, 5.0 mL of each sample was aliquotted into trace clean 16x150 glass tubes with PTFE lined caps (VWR International), 5.0 mL digestion reagent was then added (10 g potassium persulfate, 6 g boric acid, and 3 g NaOH in 1000mL Millipore water) and samples were autoclaved in a Tuttnauer Brinkman autoclave (Westbury, NY). After digestion and sample cooling, the total phosphorus concentrations were determined spectrophotometrically on the PE Spec using HACH PhosVer3 packets (Loveland, CO). The limit of detection for this analysis was 0.06 mg/L Tot-P.

Results

Summary of QC samples

Two major quantitative means were used to evaluate the performance of the laboratories and field crew. The first was routine measurement of QC samples, the second was the evaluation of independently prepared performance check samples. The summary of the QC samples run in conjunction with sample collection does not address the actual values or trends in the samples collected. The QC data collected addresses the precision, accuracy, and the overall confidence in the produced data set.

For the 2005-2007 sample years, EERP and UCD laboratories had an overall QC sample pass rate of 97%. This included all the required QC samples: calibration checks, laboratory check samples, analytical and field duplicates, matrix spikes, and blanks run in conjunction with the unknown samples. Average for the QC sample pass rates for each individual analysis is shown in Table 2 for EERP and Table 3 for UCD.

Shown in Table 4 are the Field QC samples, including both the pre and post calibration standards. These numbers represent an average of 9 different sonde units used throughout 2005 - 2007. The overall passage of QC samples for the field was 97.5 %.

Outside blind check samples (Ultra Scientific, North Kingstown, RI; RTC, Laramie, WY) were purchased for an additional assessment of the laboratory capabilities. This allows the analyst to address any weaknesses and provides a quality check from an independent source. From 2005 to 2007, all of the proficiency check standards were analyzed within acceptable limits as defined by the supplier with the exception of those highlighted in orange (see Table 5 and 6). In 2006 a sample was analyzed by both the EERP and UC Davis laboratories which produced 48.3 and 55.1 % recoveries for TN, respectively. Upon investigation it was discovered that this standard was made from Glycine. Analysts at EERP prepared Glycine standards and confirmed that this compound is not efficiently analyzed by our techniques. Ongoing method development has addressed this issue and now this compound is analyzed efficiently. Two TN samples analyzed by UCD in 2007 had low recoveries (DO-75-040507 and DO-75-120607), were high in TN, and outside the range of UCD analysis.

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Table 1: Definition of Analytical Quality Control samples used in laboratory analysis

| QC Type | Definition | Frequency | Used to Evaluate | Limits | Corrective Action |
|---|--|---|--|------------------------------------|--|
| Calibration Check (CC) | Standard solution at a concentration in the center of the calibration curve. | Every analytical batch or at least every 20 samples. | Accuracy Comparability | 80 –120% | Analysis can not proceed unless the CC passes. |
| Laboratory Control Sample (LCS) | Standard solution from a different vendor than that of the calibration standard spiked with compounds of interest into a clean water matrix. | Every analytical batch or at least every 40 samples. | Accuracy Comparability | 80 –120% | Perform instrument maintenance and prepare new standard solution if necessary. |
| Matrix spike & Matrix spike duplicate (MS/MSD) | Standard solution with compounds of interest spiked into a representative sample matrix. | Every 40 samples. | Precision Accuracy Comparability | 80 –120% | If LCS passes, result may reflect matrix interference and may be reported with qualification. |
| Surrogate | The addition of a non-occurring substituted compound to the sample matrix. | Inorganics: Not Applicable. Organics: every sample if available. | Precision Comparability | 75 –125% | Rerun sample. If second result is not within limits, report with qualifier. |
| Instrument or Analytical Blank (IB or AB) | Clean water matrix, free of analyte. Analyzed in same manner as samples. | Every analytical batch or at least every 20 samples. | Accuracy | Below Method Detection Limit (MDL) | In some cases, target compound values may be subtracted out, in other analyses target compounds present in blank must be flagged as contamination and may not be subtracted out. |

Table 2: Summary of Quality Control samples for the EERP laboratory analyses, 2005-2007

| | QA/QC type PQL (mg/L) | Total Alkalinity 2 | Ammonia-N 0.045 | Nitrate-N 0.19 | Dissolved Phosphate 0.024 | Total Iron-Fe 0.045 | Total P 0.052 | Total Protein 1.06 | Silica 0.017 |
|----------------|--------------------------|-----------------------|--------------------|-------------------|------------------------------|------------------------|------------------|-----------------------|-----------------|
| | Total | 99.87% | 93.69% | 96.71% | 96.14% | 96.20% | 100.00% | 95.56% | 100.00% |
| | LabDup | 100.00% | 97.37% | 98.72% | 98.72% | 93.59% | 100.00% | 93.75% | 100.00% |
| | Dup | 100.00% | 92.02% | 94.87% | 85.51% | 89.24% | 100.00% | 88.44% | 100.00% |
| % of QA passed | MS | 100.00% | 88.03% | 92.09% | 97.22% | 97.22% | 100.00% | 97.44% | 100.00% |
| | MSD | 99.07% | 86.99% | 91.28% | 93.94% | 96.97% | 100.00% | 96.46% | 100.00% |
| | LCS | 100.00% | 95.48% | 100.00% | 100.00% | 100.00% | 100.00% | 92.86% | 100.00% |
| | CC | 100.00% | 96.76% | 100.00% | 97.62% | 96.37% | 100.00% | 100.00% | 100.00% |
| | TB (<PQL) | 100.00% | 99.15% | 100.00% | 100.00% | 100.00% | 100.00% | 100.00% | 100.00% |

| | QA/QC type PQL (mg/L) | (TOC) 0.4872 | Total Nitrogen (TN) | (DOC) 0.4872 | Disolved Nitrogen (DN) | Total N (Timberline) 0.1500 | BOD 1 | CBOD 1 | NBOD 1 |
|----------------|--------------------------|-----------------|---------------------|-----------------|------------------------|--------------------------------|---------------|---------------|---------------|
| | Total | 95.35% | 99.40% | 97.46% | 99.03% | 100.00% | 96.85% | 96.31% | 88.99% |
| | LabDup | 99.06% | 98.57% | 98.72% | 100.00% | 100.00% | 95.00% | 97.50% | 80.00% |
| | Dup | 93.72% | 98.61% | 95.27% | 100.00% | 100.00% | 97.41% | 92.37% | 88.82% |
| % of QA passed | MS | 95.26% | 100.00% | 95.83% | 98.61% | 100.00% | | | |
| | MSD | 95.04% | 100.00% | 95.83% | 97.37% | 100.00% | | | |
| | LCS | 96.30% | 100.00% | 100.00% | 100.00% | 100.00% | | | |
| | CC | 92.48% | 100.00% | 99.15% | 98.61% | 100.00% | | | |
| | TB (<PQL) | 95.61% | 98.61% | 97.44% | 98.6% | 100.00% | 98.15% | 99.07% | 98.15% |

| | QA/QC type PQL (mg/L) | (TSS) 5 mg | (VSS) 5 mg | Chl-a SM UV abs < 0.1 | Phaeophyton abs < 0.1 | Chl-a SM UV & Phaeophyton Total abs < 0.1 | Chl-a TriChrom abs < 0.1 | Chl-b TriChrom abs < 0.1 | Chl-c TriChrom abs < 0.1 |
|----------------|--------------------------|---------------|---------------|--------------------------|--------------------------|--|-----------------------------|-----------------------------|-----------------------------|
| | Total | 94.75% | 92.01% | 86.26% | 82.03% | 86.07% | 86.07% | 78.65% | 81.90% |
| | LabDup | | | | | | | | |
| | Dup | 89.50% | 85.74% | 72.52% | 64.05% | 72.14% | 72.14% | 57.30% | 63.81% |
| % of QA passed | MS | | | | | | | | |
| | MSD | | | | | | | | |
| | LCS | | | | | | | | |
| | CC | | | | | | | | |
| | TB (<PQL) | 100.00% | 98.29% | 100.00% | 100.00% | 100.00% | 100.00% | 100.00% | 100.00% |

Table 3: Summary of the Quality Control samples for the UC Davis laboratory analyses

| | QA Parameter | Total Number of Each Parameter Analyzed | Total N (mg/L) | NH4-N (mg/L) | NO3-N (mg/L) | Total P (mg/L) | PO4-P (mg/L) |
|-----------------|------------------|---|----------------|-----------------|--------------|-------------------|-----------------|
| | | | PQL<0.05 | PQL<0.01 | PQL<0.01 | PQL<0.005 | PQL<0.003 |
| % of QA Passing | Field Duplicate | 119 | 97.48% | 88.24% | 96.64% | 95.80% | 95.80% |
| | Laboratory Blank | 20 | 100.00% | 100.00% | 100.00% | 90.00% | 80.00% |
| | Trip Blank | 122 | 94.26% | 95.90% | 98.36% | 95.08% | 93.44% |
| | Total | 261 | 96.17% | 92.72% | 97.70% | 95.02% | 93.49% |

Sonde Paramater

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Table 5: EERP and UC Davis Nutrient Proficiency Check sample results

| mg/L NO3 - N | | | mg/L NO3 - N | | | % recovery UOP | %recovery UCD | |
|---------------|-----------------------------------|-------------|-------------------------------------|-------------------------------|-------------------------|----------------|-------------------------|-------|
| Sample ID | Catalog number (ultra scientific) | Code number | Expected concentration mg/L NO3 - N | Acceptable Range mg/L NO3 - N | UOP result mg/L NO3 - N | | UCD result mg/L NO3 - N | |
| DO-70-060806 | QCI-757A | 72039 | 6.92 | 6.23-7.61 | 6.57 | 94.9 | na | |
| DO-70-100605 | QCI-757A | 75240 | 3.81 | 3.43-4.19 | 4.34 | 113.9 | na | |
| DO-72-030206 | QCI-7110 | 79198 | 8.48 | 7.21-9.63 | 7.78 | 91.7 | na | |
| DO-72-060806 | QCI-7110 | 76260 | 10.2 | 8.7-11.6 | 8.93 | 87.5 | na | |
| DO-72-100605 | QCI-7110 | 75568 | 5.42 | 4.64 - 6.10 | na | | 5.231 | 96.5 |
| DO-72-101906 | QCI-7110 | 78633 | 12.3 | 10.5-14.0 | 10.6 | 86.2 | 12.52 | 101.8 |
| DO-72-040507 | QCI-7110 | 78638 | 5.25 | 4.47-5.98 | n/a | | 5.175 | 98.6 |
| DO-72-120607 | QCI-7110 | 72427 | 2.06 | 1.75-2.36 | 2.22 | 107.8 | n/a | |
| DO-74-030206 | QCI-745A | 78379 | 38.8 | 33.3-43.5 | 33.91 | 87.4 | 37.34 | 96.2 |
| DO-74-060806 | QCI-745A | 74597 | 34.6 | 29.8-38.8 | 29.41 | 85.0 | n/a | |
| DO-74-040507 | QCI-745A | 76967 | 22.2 | 18.9-25.2 | 23.84 | 107.4 | 24.336 | 109.6 |
| DO-74-120607 | QCI-745A | 71708 | 34.6 | 29.5-39.3 | 34.16 | 98.7 | 30.41 | |
| mg/L NH4 - N | | | mg/L NH4 - N | | | % recovery UOP | UCD result mg/L NH4 - N | |
| Sample ID | Catalog number (ultra scientific) | Code number | Expected concentration mg/L NH4 - N | Acceptable Range mg/L NH4 - N | UOP result mg/L NH4 - N | | | |
| DO-74-030206 | QCI-745A | 78379 | 18.3 | 15.6-20.9 | 19.83 | 108.4 | 18.06 | 98.7 |
| DO-74-060806 | QCI-745A | 74597 | 10.5 | 8.9-12.0 | 10.06 | 95.8 | n/a | |
| DO-74-101906 | QCI-745A | 71269 | 13.1 | 10.8-15.2 | 14.31 | 109.2 | 15.72 | 120.0 |
| DO-74-040507 | QCI-745A | 76967 | 18.3 | 15.2-21.1 | 16.71 | 91.3 | 18.865 | 103.1 |
| DO-74-120607 | QCI-745A | 71708 | 10.5 | 8.6-12.2 | 9.22 | 87.8 | 10.15 | 96.7 |
| DO-205-040507 | QCI-042-1 | 10611 | 2.02 | 1.49-2.55 | 1.57 | 77.7 | 1.751 | 86.7 |
| mg/L PO4 - P | | | mg/L PO4 - P | | | % recovery UOP | UCD result mg/L PO4 - P | |
| Sample ID | Catalog number (ultra scientific) | Code number | Expected concentration mg/L PO4 - P | Acceptable Range mg/L PO4 - P | UOP result mg/L PO4 - P | | | |
| DO-74-030206 | QCI-745A | 78379 | 4.71 | 4.26-5.20 | 4.91 | 104.2 | 5.079 | 107.8 |
| DO-74-101906 | QCI-745A | 71269 | 1.18 | 1.01-1.37 | 1.24 | 105.1 | 1.147 | 97.2 |
| DO-74-040507 | QCI-745A | 76967 | 4.71 | 4.17-5.29 | 4.97 | 105.5 | 1.414 | 30.0 |
| DO-74-120607 | QCI-745A | 71708 | 2.06 | 1.80-2.35 | 2.09 | 101.5 | 2.009 | 97.5 |
| DO-205-040507 | QCI-042-1 | 10611 | 0.74 | 0.615-0.871 | 0.72 | 97.3 | 0.655 | 88.5 |
| TOTAL P | | | TOTAL P | | | % recovery UOP | UCD result mg/L P | |
| Sample ID | Catalog number (ultra scientific) | Code number | Expected concentration mg/L P | Acceptable Range mg/L P | UOP result | | | |
| DO-75-030206 | QCI-745B | 78842 | 5.07 | 4.20-5.59 | na | | 5.477 | 108.0 |
| DO-75-101906 | QCI-745B | 77428 | 3.04 | 2.66-3.46 | na | | 3.306 | 108.8 |
| DO-75-040507 | QCI-745B | 78237 | 5.07 | 4.47-5.72 | 9.2368 | 182.2 | 4.904 | 96.7 |
| DO-75-120607 | QCI-745B | 71050 | 2.03 | 1.76-2.34 | 1.6871 | 83.1 | 1.901 | 93.6 |
| TOTAL N | | | TOTAL N | | | % recovery UOP | UCD result mg/L N | |
| Sample ID | Catalog number (ultra scientific) | Code number | Expected concentration mg/L N | Acceptable Range mg/L N | UOP result mg/L N | | | |
| DO-72-101906 | QCI-7110 | 78633 | 12.3 | 10.5-14.0 | 12.87 | 104.6 | 12.86 | 104.6 |
| DO-72-040507 | QCI-7110 | 78638 | 5.25 | 4.47-5.98 | na | | 4.77 | 90.9 |
| DO-74-101906 | QCI-745A | 71269 | 20 | 5.9-7.9 | na | | 19.40 | 97.0 |
| DO-74-040507 | QCI-745A | 76967 | 40.5 | 34.1-46.3 | 41.25 | 101.9 | 43.71 | 107.9 |
| DO-74-120607 | QCI-745A | 71708 | 45.1 | 38.1-51.5 | 46.21 | 102.5 | 39.51 | 87.6 |
| DO-75-030106 | QCI-745B | 78842 | 16.8 | 13.7-19.4 | na | | 16.61 | 98.9 |
| DO-75-101906 | QCI-745B | 77428 | 33.6 | 25.6-39.6 | 16.24 | 48.3 | 18.50 | 55.1 |
| DO-75-040507 | QCI-745B | 78237 | 16.8 | 12.9-19.9 | 16.17 | 96.3 | 12.08 | 71.9 |
| DO-75-120607 | QCI-745B | 71050 | 18.7 | 14.3-22.1 | 17.62 | 94.3 | 11.99 | 64.1 |
| DO-200-030107 | made in-house | na | 3.5 | +/- 20% | 3.40 | 97.1 | 3.51 | 100.3 |
| DO-201-030107 | made in-house | na | 6.8 | +/- 20% | 6.56 | 96.5 | 5.53 | 81.3 |
| DO-202-030107 | made in-house | na | 1.4 | +/- 20% | 1.49 | 106.4 | 1.46 | 104.3 |
| TSS | | | TSS | | | % recovery UOP | | |
| Sample ID | Catalog number (ultra scientific) | Code number | Expected concentration mg/L | Acceptable Range mg/L | UOP result mg/L | | | |
| DO-73-030206 | QCI-711 | 77754 | 151 | 134-159 | 145.2 | 96.2 | | |
| DO-73-062906 | QCI-711 | 70362 | 161 | 143-169 | 150.97 | 93.8 | | |
| DO-73-100605 | QCI-711 | 78352 | 164 | 138-170 | 156.11 | 95.2 | | |
| DO-73-101906 | QCI-711 | 72853 | 159 | 142-167 | 163.46 | 102.8 | | |
| DO-73-040507 | QCI-711 | 74747 | 120 | 106-132 | 122 | 101.7 | | |

Table 6: EERP Nutrient Proficiency Check sample results

| TSS | | | TSS | | | |
|--------------|--------------------------------------|-------------|--------------------------------|--------------------------|--------------------|-------------------|
| Sample ID | Catalog number (ultra scientific) | Code number | Expected concentration mg/L | Acceptable Range mg/L | UOP result mg/L | % recovery UOP |
| DO-73-030206 | QCI-711 | 77754 | 151 | 134-159 | 145.2 | 96.2 |
| DO-73-062906 | QCI-711 | 70362 | 161 | 143-169 | 150.97 | 93.8 |
| DO-73-100605 | QCI-711 | 78352 | 164 | 138-170 | 156.11 | 95.2 |
| DO-73-101906 | QCI-711 | 72853 | 159 | 142-167 | 163.46 | 102.8 |
| DO-73-040507 | QCI-711 | 74747 | 120 | 106-132 | 122 | 101.7 |
| DO-73-120607 | QCI-711 | 72255 | 21.9 | 16.2-25.2 | 17.53 | 80.0 |

| TOC | | | TOC | | | |
|--------------|--------------------------------------|-------------|--------------------------------|--------------------------|--------------------|-------------------|
| Sample ID | Catalog number (ultra scientific) | Code number | Expected concentration mg/L | Acceptable Range mg/L | UOP result mg/L | % recovery UOP |
| DO-76-030206 | QCI-731 | 77276 | 35.3 | 31.0-39.7 | 37.11 | 105.1 |
| DO-76-030206 | QCI-731 | 77276 | 35.3 | 31.0-39.7 | 35.44 | 100.4 |
| DO-76-060806 | QCI-731 | 75955 | 28.2 | 25.0-31.2 | 25.2 | 89.4 |
| DO-76-101906 | QCI-731 | 70488 | 47 | 41.8-51.8 | 51.9 | 110.4 |
| DO-76-040507 | QCI-731 | 73280 | 47 | 41.8-51.8 | 31.854 | 67.8 |
| DO-76-120607 | QCI-731 | 74810 | 28.2 | 25.0-31.2 | 28.28 | 100.3 |
| DO-78-092706 | QCI-026 | 10445 | 14.1 | 11.6-16.6 | 15.054 | 106.8 |

| Conductivity | | | Conductivity | | | |
|---------------------|---------|-------|------------------------|------------------|------------|-------------------|
| | | | Expected concentration | Acceptable Range | UOP result | % recovery UOP |
| DO-72-060806 | QCI-710 | 76260 | 940 | 884-997 | 932 | 99.1 |
| DO-72-101906 | QCI-710 | 78633 | 814 | 764-864 | 851 | 104.5 |
| DO-72-042607 | QCI-710 | 78638 | 1350 | 1270-1430 | 1370 | 101.5 |
| DO-72-120607 | QCI-710 | 72427 | 1470 | 1390-1550 | 1465 | 99.7 |

| pH | | | pH | | | |
|-------------------------------|---------|-------|-----------|-----------|------------|--|
| | | | | | | |
| DO-72-060806 lab result | QCI-710 | 76260 | 9.23 | 9.03-9.43 | 9.18 | |
| DO-72-060806 field result | QCI-710 | 76260 | 9.23 | 9.03-9.43 | 9.15 | |
| DO-72-101906 field (sonde) | QCI-710 | 78633 | 9.28 | 9.08-9.48 | 9.13 | |
| DO-72-040507 field (sonde) | QCI-710 | 78638 | 9.16 | 8.96-9.36 | 8.89, 8.92 | |
| DO-72-120607 field (sonde) | QCI-710 | 72427 | 9.19 | 8.99-9.39 | 9.04, 9.06 | |

| BOD | | | BOD | | | |
|--------------|--------------------------------------|-------------|--------------------------------|--------------------------|--------------------|-------------------|
| Sample ID | Catalog number (ultra scientific) | Code number | Expected concentration mg/L | Acceptable Range mg/L | UOP result mg/L | % recovery UOP |
| DO-78-092706 | QCI-026 | 10445 | 22.2 | 10.9-33.4 | 28.75 | 129.5 |
| DO-78-040507 | QCI-026 | 10647 | 26.1 | 12.9-39.3 | 34.6 | 132.6 |

| CBOD | | | CBOD | | | |
|--------------|--------------------------------------|-------------|--------------------------------|--------------------------|--------------------|-------|
| Sample ID | Catalog number (ultra scientific) | Code number | Expected concentration mg/L | Acceptable Range mg/L | UOP result mg/L | |
| DO-78-092706 | QCI-026 | 10445 | 19.2 | 8.56-29.8 | 28.5 | 148.4 |
| DO-78-040507 | QCI-026 | 10647 | 22.7 | 10.1-35.0 | 34 | 149.8 |

| ALKALINITY | | | ALKALINITY | | | |
|-------------------|--------------------------------------|-------------|---|---|-------------------------------------|-------------------|
| Sample ID | Catalog number (ultra scientific) | Code number | Expected concentration mg CO ₃ /L | Acceptable Range mg CO ₃ /L | UOP result mg CO ₃ /L | % recovery UOP |
| DO-72-030206 | QCI-710 | 79198 | 352 | 327-363 | 328 | 93.2 |
| DO-72-060806 | QCI-710 | 76260 | 231 | 208-254 | 239 | 103.5 |
| DO-72-100605 | QCI-710 | 75568 | 538 | 511-555 | 514 | 95.5 |
| DO-72-101906 | QCI-710 | 78633 | 249 | 224-274 | 234 | 94.0 |
| DO-72-042607 | QCI-710 | 78601 | 352 | 327-363 | 333 | 94.6 |
| DO-72-120607 | QCI-710 | 72427 | 146 | 132-161 | 134 | 91.8 |